Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Frenkel Biexcitons

David Fox [a]
[a] Department of Physics, State University of New York at Stony Brook, Stony Brook, N.Y., 11794, U.S.A

Version of record first published: 14 Oct 2011.

To cite this article: David Fox (1980): Frenkel Biexcitons, Molecular Crystals and Liquid Crystals, 57:1, 39-45

To link to this article: http://dx.doi.org/10.1080/00268948008069817

Mol. Cryst. Liq. Cryst., 1980, Vol. 57, pp. 39–45
0026-8941/80/5701-0039$04.50/0

Frenkel Biexcitons

States and Transition Spectra

DAVID FOX

Department of Physics, State University of New York at Stony Brook, Stony Brook, N.Y. 11794, U.S.A.

A biexciton model is developed, valid for cases in which the excitation-transfer matrix elements are small compared with the binding energy between the two excitations. Eigenstates are found and spectroscopic transitions between biexcitons and single excitons are discussed. Observation of these transitions can be used to find values of the binding energy and of the excitation-transfer energies.

Interactions between excitons, if attractive, can lead to the formation of polyexcitons. At high concentrations and low temperatures, there can be a phase transition from a vapor of single excitons and polyexcitons to a liquid whose particles are molecular excitations, more or less localized. Of these configurations, the simplest to deal with, both experimentally and theoretically, is the biexciton. A study of spectroscopic transitions between biexciton and single exciton states can yield information about the interactions, as well as about the excitation transfer (resonance) matrix elements.

To the author's knowledge, biexcitons have never been observed. In another paper[1] (hereinafter called A) experimental difficulties in observing polyexcitons and condensation are discussed, together with suggested procedures for overcoming these difficulties. Perhaps the most serious problem, with certain crystals, is the very short lifetime of pairs of neighboring excitations resulting from exciton-exciton annihilation. Where the lowest excited molecular electronic state has less than half the excitation energy of the next higher state, the life-time of biexcitons may be determined by the radiative lifetime of a single excitation. With careful choice of crystals and of the conditions of the experiment, it seems likely that biexcitons can be found.

In A, a formalism is developed for the calculation of emission and absorption spectra of polyexcitons and excitonic liquid. For biexcitons, in the approximation adopted here (valid for the most favourable condition for observing biexcitons) a much simpler procedure is applicable and will be used. Detailed calculations, as well as investigations of corrections to the model, are best left for a time when experimental data are available. This brief account is intended mainly as a guide in the interpretation and analysis of the spectra in future experiments.

Consider a crystal in which the tight-binding (Frenkel) limit is appropriate. For the general polyexciton problem, a set of basis states is adopted, each containing n localized excitations (particles), with $n = 0, 1, 2 \ldots$. One such state is designated by $|\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n\rangle$, where $\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n$ are the positions of the excited molecules.

In this basis, the diagonal terms of the Hamiltonian H have two contributions: (1) the excitation energy ("rest energy") $n\varepsilon$ for each n-particle state, where ε is the energy expectation value of a single isolated excitation, and (2) a sum of pairwise interaction terms, with $I_{\mathbf{rs}}$ designating the energy of interaction between particles at **r** and **s**.

An off-diagonal element of H between two states of the same n is nonzero if and only if the initial and final states are identical except for the transfer of a single particle from one site to another (say, **r** to **s**); in this case, the element equals $K_{\mathbf{rs}}$, which is equal to the excitation transfer matrix element between the single-particle states $|\mathbf{r}\rangle$ and $|\mathbf{s}\rangle$.

Matrix elements between states of different n can be of the same order of magnitude as $K_{\max}$ (the largest $|K_{\mathbf{rs}}|$) but they connect states which differ in energy by at least ε. In the crystals to which the present development is most likely to be applied, ε is very much larger than $K_{\max}$, so one can generally ignore the mixing of states with different n. Therefore, for the problem of transitions between biexcitons and single excitons, with emission of photons, only $n = 1$ and $n = 2$ states need be considered. In this limited basis, the only nonvanishing matrix elements are of the form

$$\langle \mathbf{r}|H|\mathbf{r}\rangle = \varepsilon, \tag{1}$$

$$\langle \mathbf{r}|H|\mathbf{s}\rangle = K_{\mathbf{rs}}, \tag{2}$$

$$\langle \mathbf{r}, \mathbf{s}|H|\mathbf{r}, \mathbf{s}\rangle = 2\varepsilon + I_{\mathbf{rs}}, \tag{3}$$

$$\langle \mathbf{r}, \mathbf{r}'|H|\mathbf{s}, \mathbf{r}'\rangle = K_{\mathbf{rs}}, \tag{4}$$

with $\mathbf{r} \neq \mathbf{s}$ in each of the last three equations.

Comparison of the expressions in A for $I_{\mathbf{rs}}$ and for the gas-to-crystal shift $\Delta\varepsilon$ suggest that, while $I_{\max}$ (the largest $|I_{\mathbf{rs}}|$) is likely to be smaller than $\Delta\varepsilon$, it may well be less than an order of magnitude smaller. In nonpolar crystals, one can expect values of $I_{\max}$ as large as $\sim 100\ \text{cm}^{-1}$. In crystals of those polar molecules with very large changes in dipole moment between ground and excited states,[1] $I_{\max}$ can be much larger than $100\ \text{cm}^{-1}$.

We restrict our attention now to those $I_{\mathbf{rs}}$ which are negative (although the formalism is valid for repulsive pair states as well). It is shown in A that the most favorable condition for binding is $|I_{\mathbf{rs}}| \gg K_{\max}$. We consider only this case. If I_1 and I_2 are unequal values of two of the largest $|I_{\mathbf{rs}}|$, with $I_2 > I_1$, then, with occasional exceptions, $\Delta I \equiv I_2 - I_1$ will be of the order of I_2, so that ΔI is also much greater than $K_{\max}$. We can therefore ignore the mixing of pair states with different interaction energies and apply degenerate perturbation theory to each set of symmetry-equivalent pairs, which must have the same $I_{\mathbf{rs}}$ values. The procedure to be followed is somewhat similar to that used to obtain the single-exciton eigenstates in crystals with more than one molecule per unit cell.[2] It will be recalled that this diagonalization is usually carried out in two steps. First, a "one-site exciton" is formed from each set of translationally-equivalent local states:

$$|\mathbf{k}, \alpha\rangle = N^{-1/2} \sum_{\mathbf{r}_\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}_\alpha)|\mathbf{r}_\alpha\rangle \tag{5}$$

where the index α designates one sublattice; N is the number of unit cells in the sample. The basis $|\mathbf{k}, \alpha\rangle$ partly diagonalizes the single-exciton block in H. In the second step, diagonalization is completed by mixing states with the same $\mathbf{k}$ and al lα.

Similarly, "one-bond biexcitons" can be formed from translationally-equivalent localized pair states:

$$|\mathbf{k}, \mathbf{s}\rangle = N^{-1/2} \sum_{\mathbf{r}} \exp[\mathbf{k} \cdot (\mathbf{r} + \tfrac{1}{2}\mathbf{s})]|\mathbf{r}, \mathbf{r} + \mathbf{s}\rangle \tag{6}$$

(Inclusion of the overall phase factor $e^{(1/2)i\mathbf{k}\cdot\mathbf{s}}$ has the effect of determining the phase of each term at the center of mass of the pair. This symmetric choice leads to real matrix elements of H, somewhat simplifying computer programming.) In the second step, one mixes the set of states with the same $\mathbf{k}$ and all factor-group equivalents of the bond vector $\mathbf{s}$.

The restriction on pair states which can be mixed (Eq. (4)) leads to a feature not present in single excitons. The effect of this restriction on the mixing of states can be visualized by the following geometric construction: The matrix element $\langle \mathbf{r}, \mathbf{r}'|H|\mathbf{s}, \mathbf{r}'\rangle$ is represented by a pair of bonds; the final bond (between $\mathbf{r}$ and $\mathbf{r}'$) is obtained by flipping the initial one (between $\mathbf{s}$ and $\mathbf{r}'$) into a symmetry-equivalent position, keeping the end at $\mathbf{r}'$ fixed. Continuing in this way, with all permitted flips, one gets a network of bonds which are connected, directly or indirectly, by nonvanishing matrix elements. Only these bonds need be mixed to form a set of eigenstates; if there are equivalent bonds not in the first network, they will form one or more additional sets of eigenstates, with all sets having a common eigenvalue distribution.

In a crystal with three inequivalent axes, an extreme example is provided by the network generated from the pair $|\mathbf{r}, \mathbf{r} + \mathbf{s}\rangle$, with $\mathbf{s}$ parallel to one of the axes (say a) and with both particles on the same sublattice. The inequivalence of the axes shows that all bonds in the set equivalent to the initially chosen one are also parallel to the a-axis; they are, of course, of equal length. Then an entire network consists of a single line of bonds connecting sites $\mathbf{R} + m\mathbf{s}$, where $\mathbf{R}$ is a mixed vector and m is an integer. The pairs in this network combine to form one-dimensional biexcitons, of the form of Eq. (6) but with one-dimensional $\mathbf{k}$ and with $\mathbf{r}$ restricted to $\mathbf{R} + m\mathbf{s}$. If $\mathbf{s} = p\mathbf{a}$, and $p > 1$, there will be sites on the same line which cannot be reached by the flipping process, so that there will be p similar sets of biexciton states on the same line, as well as on every parallel line of each sublattice. Since corresponding states of different networks are degenerate in energy, one may choose arbitrary combinations as eigenstates. For calculation of transition probabilities (below) it is convenient to choose combinations that give states of the three-dimensional form in Eq. (6). The energy $E_{\mathbf{k},\mathbf{s}}$ of such a state depends only on the a-component of $\mathbf{k}$. Eqs. (3), (4), and (6) yield

$$E_{\mathbf{k},\mathbf{s}} = 2\varepsilon + I_{\mathbf{s}} + 2K_{2\mathbf{s}} \cos \mathbf{k} \cdot \mathbf{s} \tag{7}$$

where $I_{\mathbf{s}} \equiv I_{0,\mathbf{s}}$, $K_{2\mathbf{s}} \equiv K_{0,2\mathbf{s}}$; the zero subscript designates the origin molecule. Translational symmetry has been used to replace $I_{\mathbf{rr}'}$ by $I_{0,\mathbf{r}-\mathbf{r}'}$ and $K_{\mathbf{rr}'}$ by $K_{0,\mathbf{r}-\mathbf{r}'}$. It should be noted that, as a result of the restriction implied in Eq. (4), only $K_{2\mathbf{s}}$ appears in Eq. (7), in contrast with the sum containing all $K_{\mathbf{r}}$ in the energy of a single exciton.

In crystals of low symmetry, one can form linear biexcitons from any $\mathbf{s}$ lying totally on one sublattice. With sufficiently high symmetry, there will be bonds equivalent to $\mathbf{s}$ on the same sublattice but not parallel to $\mathbf{s}$. The network will then be two or three dimensional, but still lying on one sublattice, and one can choose eigenstates which are totally restricted to that network, with degenerate equivalents appearing on the other sublattices.

For small $K_{\max}$, the largest $K_{2\mathbf{s}}$ may be too small to detect. In high-resoltion measurements of the largest $K_{\mathbf{r}}$ in naphthalene,[3] Hanson could not detect $K_{2\mathbf{s}}$ for any $\mathbf{s}$ lying on one sublattice. Eq. (7) shows that under such circumstances, $E_{\mathbf{k},\mathbf{s}}$ is effectively independent of $\mathbf{k}$. This degeneracy can be used to explore the single-exciton band, as discussed below.

If the bond vector connects two sublattices, the network of bonds may or may not include all sites, but one cannot choose eigenstates on a single sublattice. Consider, for example, a naphthalene-like structure with two molecules per unit cell, one at (0, 0, 0) and one at ($\frac{1}{2}a$, $\frac{1}{2}b$, 0). Define $\mathbf{u} \equiv \frac{1}{2}(\mathbf{a} + \mathbf{b})$; $\mathbf{v} \equiv \frac{1}{2}(\mathbf{a} - \mathbf{b})$. One complete set of equivalent bond vectors is $\mathbf{u}, -\mathbf{u}, \mathbf{v}, -\mathbf{v}$, where we adopt the convention that the tail of each of these vectors is at a molecule on sublattice *I* and the head on *II*. The network includes sites on both *I* and *II*, but only in the ab-plane, as the definitions of $\mathbf{u}$ and $\mathbf{v}$ show. Here the two-step procedure for diagonalizing H is appropriate. Four one-bond biexcitons are formed, each as in Eq. (6), with **s** replaced successively by **u**,−**u**, **v**, and−**v**. In the new representation, H is partially diagonalized, with off-diagonal elements remaining only in 4 × 4 blocks corresponding to the four one-bond states with the same **k**. The elements of these blocks are readily calculated from Eqs. (3), (4), and (6). These equations lead to

$$\langle \mathbf{k}, \mathbf{w} | H | \mathbf{k}, \mathbf{w}' \rangle = (2\varepsilon + I_{\mathbf{w}})\delta_{\mathbf{w},\mathbf{w}'} + K_{\mathbf{w}-\mathbf{w}'}\gamma_{\mathbf{k},\mathbf{w}-\mathbf{w}'}(1 - \delta_{\mathbf{ww}'}) \tag{8}$$

where $\gamma_{\mathbf{k},\mathbf{x}} = 2\cos\frac{1}{2}\mathbf{k}\cdot\mathbf{x}$ and $\mathbf{w}, \mathbf{w}' = \mathbf{u}, -\mathbf{u}, \mathbf{v}$, or $-\mathbf{v}$. The 4 × 4 **k**-block is then $H_{\mathbf{k}} = (2\varepsilon + I_{\mathbf{u}})\mathbf{1} + H_{K,\mathbf{k}}$, where **1** is the 4 × 4 unit matrix and

$$H_{K,\mathbf{k}} = \begin{pmatrix} 0 & K_{2\mathbf{u}}\gamma_{\mathbf{k},2\mathbf{u}} & K_{\mathbf{b}}\gamma_{\mathbf{k},\mathbf{b}} & K_{\mathbf{a}}\gamma_{\mathbf{k},\mathbf{a}} \\ K_{2\mathbf{u}}\gamma_{\mathbf{k},2\mathbf{u}} & 0 & K_{\mathbf{a}}\gamma_{\mathbf{k},\mathbf{a}} & K_{\mathbf{b}}\gamma_{\mathbf{k},\mathbf{b}} \\ K_{\mathbf{b}}\gamma_{\mathbf{k},\mathbf{b}} & K_{\mathbf{a}}\gamma_{\mathbf{k},\mathbf{a}} & 0 & K_{2\mathbf{v}}\gamma_{\mathbf{k},2\mathbf{v}} \\ K_{\mathbf{a}}\gamma_{\mathbf{k},\mathbf{a}} & K_{\mathbf{b}}\gamma_{\mathbf{k},\mathbf{b}} & K_{2\mathbf{v}}\gamma_{\mathbf{k},2\mathbf{v}} & 0 \end{pmatrix} \tag{9}$$

Again only a small number of $K_{\mathbf{x}}$ appear, for the same reason as in Eq. (7). If $K_{2\mathbf{u}}$ and $K_{2\mathbf{v}}$ are negligible, the symmetry of the approximate H is higher than that of the crystal, and each of the 4 × 4 matrices may be diagonalized by the same unitary transformation

$$U = \frac{1}{2}\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \tag{10}$$

The energies (with the states in order of the rows of U) are $2\varepsilon + I_{\mathbf{u}} + \gamma_{\mathbf{a}} + \gamma_{\mathbf{b}}$, $2\varepsilon + I_{\mathbf{u}} - \gamma_{\mathbf{a}} - \gamma_{\mathbf{b}}$, $2\varepsilon + I_{\mathbf{u}} - \gamma_{\mathbf{a}} + \gamma_{\mathbf{b}}$, and $2\varepsilon + I_{\mathbf{u}} + \gamma_{\mathbf{a}} - \gamma_{\mathbf{b}}$. If $K_{2\mathbf{u}}$ is not negligible, then U is replaced by a **k**-dependent matrix. In naphthalene,[3] $K_{\mathbf{a}}$ and $K_{\mathbf{b}}$ are of the order of 5 cm^{-1}; $K_{2\mathbf{u}}$ is negligible.

Transitions can take place from a biexciton to a single exciton with the emission of a photon. In contrast with the sharp Davydov emission spectrum of the singles,[2] biexciton emission is a band-to-band transition and is therefore broad, with width of the order of several times $K_{\max}$. Band-to-band transitions have been observed between electronic and vibrational excitons, both single.[4] Where the width of the vibrational exciton band is negligibly small, the transitions may be used to measure the density of states of the electronic band. In a similar way, emission from a degenerate biexciton band can be used to study the singles band, with one advantage over the older procedure. With the older method, it is difficult to study the top of the singles band. If emission is used, the top of the band can be observed only at relatively high temperatures, at which phonon broadening interferes with the observation.

To use absorption, the temperature must be high enough to populate the vibrational state appreciably, again leading to phonon effects. If the initial states are in a degenerate biexciton band, the emission spectrum will be independent of the temperature T over a range of low T; furthermore, there is no bias against the upper states of the lower band. (There is, however, a transition-probability weighting, discussed below.) Emission from a biexciton band of nonzero energy will depend on the structure of both bands and is T-dependent.

Calculations of transition probabilities are carried out by an extension of the method used for single-exciton spectra.[2] The total dipole operator

$$\mathbf{P} = \sum_{\mathbf{r}} \mathbf{p}_{\mathbf{r}} \tag{11}$$

is the sum of molecular dipole moments $\mathbf{p}_{\mathbf{r}}$. With both the initial and final states expressed as linear combinations of localized states, the transition matrix element of $\mathbf{P}$ is readily calculated by using

$$\langle \mathbf{r}, \mathbf{r}' | \mathbf{P} | \mathbf{s} \rangle = \delta_{\mathbf{r}'\mathbf{s}} \pi_{\mathbf{r}} + \delta_{\mathbf{r}\mathbf{s}} \pi_{\mathbf{r}'} \tag{12}$$

where $\pi_{\mathbf{r}}$ is the transition matrix element of $\mathbf{p}_{\mathbf{r}}$ between excited and ground states of molecule $\mathbf{r}$. Clearly, for all $\mathbf{r}$ on the same sublattice, the $\pi_{\mathbf{r}}$ are equal. As a simple example of the calculation, we take a crystal with one atom per cell and a bond vector which has no equivalents. One can form linear biexcitons in this case, but we take linear combinations of the degerate states to form the states (6). This procedure has the advantage that taking states of definite 3-vector $\mathbf{k}$ permits simple application of the momentum selection rule, which allows transitions only between states of the same $\mathbf{k}$. The single-exciton states are of the form in Eq. (5), with the index α not required. Eqs. (5), (6), and (12) lead to

$$\langle \mathbf{k}, \mathbf{s} | \mathbf{P} | \mathbf{k} \rangle = \pi \gamma_{\mathbf{k}\mathbf{s}} \tag{13}$$

The transition probability is therefore $\mathbf{k}$-dependent. No $\mathbf{k}$-dependence appears in the band-to-band transitions between single excitons involving different molecular excitations. In the latter case, each local term of the matrix element of $\mathbf{P}$ involves a transition between two states at the same site, so that the two exciton phase factors of that term cancel one another. On the other hand, the term of the matrix element in Eq. (13) that contains the local contribution of Eq. (12) has a phase factor $\exp(i\mathbf{k} \cdot \mathbf{s})$ from the single exciton and of $\exp[-\frac{1}{2}\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')]$ from the biexciton. According to Eq. (12), only $\mathbf{s} = \mathbf{r}$ and $\mathbf{s} = \mathbf{r}'$ contribute. In these terms there is only partial phase cancellation and hence the matrix element is $\mathbf{k}$-dependent. Note that Eq. (12) does not contain any $K_{\mathbf{x}}$, so the transition probability is the same function of $\mathbf{k}$ regardless of the band structure.

In other cases the calculation is similar. If the crystal has more than one molecule per cell, the equivalents of Eq. (13) will contain a π_α for each sublattice, either all in each equation or distributed over the equations for the subbands.

With state energies and transition probabilities known, the transition spectrum can be determined. The method follows that of previous calculations of band-to-band intensities[4] except for the effect of the **k**-dependence of the transition probability: For a given pair of initial and final states, with a particular **k**, the contribution to the intensity at that transition frequency is proportional to the transition probability for that **k** value, as well as to the Boltzmann factor for the initial state.

The dispersion relations of the biexciton and single-exciton bands both depend on the set of K_x values; the only new parameter in the biexciton band is the binding energy of a localized I_s, which gives a **k**-independent shift of the entire band. (The I_s values may be found in an experiment with isotopically-mixed crystals, in which one compares the energy of two excitations on neighboring traps with that of an isolated excitation on one trap.[1]) If emission from several inequivalent excitons is observed, the combined information can be used to verify, or perhaps to improve, values of the set of K_x obtained by other methods.[2,4] With sufficient duplication of information, the data can also be used to determine the accuracy of the approximations in the model.

References

1. D. Fox, *Chem. Phys.* to be published. See also references therein.
2. R. S. Knox, *Theory of Excitons*, Academic Press, New York, 1963, p. 21; D. P. Craig and S. H. Walmsley, in *Physics and Chemistry of the Organic Solid State* (D. Fox, M. M. Labes, and A. Weissberger, eds.) Interscience, New York, 1963, v. I, chap. 10; D. S. McClure, in *Solid State Physics* (F. Seitz and D. Turnbull, eds.) Academic Press, New York, 1959, v. 8, chap. 1.
3. D. M. Hanson, *J. Chem. Phys.*, **52**, 3409 (1970).
4. S. D. Colson, D. M. Hanson, R. Kopelman, and G. W. Robinson, *J. Chem. Phys.*, **48**, 2215 (1968).